

Title: **SULFUR REDUCTION IN GASOLINE AND DIESEL FUELS BY EXTRACTION/  
ADSORPTION OF REFRACTORY DIBENZOTHIOPHENES**

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Performance Period: 9/01/00 to 4/30/01

**ABSTRACT**

The removal of sulfur from gasoline and diesel fuels is an important aspect of this nation's effort to reduce pollution of the atmosphere by sulfur oxides. This reduction in sulfur has been largely accomplished by increasingly stringent restrictions on the sulfur content of these fuels. Hydrotreating is the well-developed catalytic process for removing sulfur as  $\text{H}_2\text{S}$  from the organosulfur compounds in petroleum feedstocks. The most easily desulfurized components are the thiols ( $\text{RSH}$ ) and thioethers ( $\text{R}_2\text{S}$ ). Recent improvements have yielded catalysts that are also capable of desulfurizing the thiophenes, benzothiophenes, and dibenzothiophenes. It is the hindered dibenzothiophenes ( $\text{R}_2\text{DBT}$ ) with alkyl groups in the 4- and 6-positions that are the slowest to undergo hydrodesulfurization. Moreover, it is these 4,6-disubstituted dibenzothiophenes that must be desulfurized in order to reach recently mandated sulfur levels in gasoline and diesel fuels.

Considering the lack of success in developing more effective catalysts, we propose to take a different approach to the removal of hindered dibenzothiophenes ( $\text{R}_2\text{DBT}$ ). This approach involves the use of  $\text{Ru}^{2+}$  compounds to remove  $\text{R}_2\text{DBTs}$  from feedstocks by extraction and/or adsorption. These processes would follow the conventional hydrotreating process, which would have already removed the thiols ( $\text{RSH}$ ), thioethers ( $\text{R}_2\text{S}$ ), thiophenes and benzothiophenes from the feed.

The general approach to the extraction of  $\text{R}_2\text{DBTs}$  from the stream exiting the hydrotreatment process involves contacting the hydrotreated petroleum feed with an aqueous solution of a  $\text{Ru}^{2+}$  compound  $[(\text{L})\text{Ru}(\text{H}_2\text{O})]$  that contains a ligand  $\text{L}$  that solubilizes the compound in water and increases the binding affinity of  $\text{Ru}^{2+}$  for  $\text{R}_2\text{DBTs}$ . This extraction gives the desired low-sulfur fuel feedstock. The remaining steps in the process remove the  $\text{R}_2\text{DBTs}$  from the  $\text{Ru}^{2+}$  and regenerate the  $\text{Ru}^{2+}$  for continued use. This is accomplished by pressuring the  $(\text{L})\text{Ru}(\text{DBT})$  complex with a ligating gas (such as ethylene,  $\text{CO}$ , or  $\text{N}_2$ ) that drives the  $\text{DBT}$  from the  $(\text{L})\text{Ru}(\text{DBT})$  into the alkane phase which is separated and incinerated. Release of the gas pressure results in the regeneration of the aqueous  $(\text{L})\text{Ru}(\text{H}_2\text{O})$  compound.

The reason for choosing  $\text{Ru}^{2+}$  as the adsorbing metal ion is its known ability to bind to dibenzothiophenes ( $\text{DBT}$ ). However, to this point, all of these  $\text{DBT}$  complexes contain expensive and unstable ligands such as cyclopentadiene, phosphines and  $\text{CO}$ . Thus, we seek to create  $\text{Ru}^{2+}$  complexes with inexpensive ligands such as  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . A viable extraction process will require complexes that are water-soluble, water-stable, and have inexpensive auxiliary ligands. The complex  $(\text{NH}_3)_5\text{Ru}(\text{OH}_2)^{2+}$  is known to react with thiophene in water at room temperature over a 20-30 minute period to give the  $(\text{NH}_3)_5\text{Ru}(\text{T})^{2+}$  complex. On the basis of equilibrium studies, it is expected that binding of  $\text{DBT}$  by  $(\text{NH}_3)_5\text{Ru}(\text{OH}_2)^{2+}$  will be even more favorable than that of thiophene ( $\text{T}$ ). For this reason, it is anticipated that  $\text{R}_2\text{DBT}$  molecules can be extracted from hydrotreated feeds using  $(\text{NH}_3)_5\text{Ru}(\text{OH}_2)^{2+}$ . Molecular models indicate that there are no steric interactions between the small  $\text{NH}_3$  ligands and the 4,6-methyl groups of the  $\text{Me}_2\text{DBT}$  ligand in the extracted  $(\text{NH}_3)_5\text{Ru}(\text{Me}_2\text{DBT})^{2+}$  complex. Early results of our studies show that  $(\text{NH}_3)_5\text{Ru}^{2+}$  does indeed bind to  $\text{DBT}$  and  $\text{Me}_2\text{DBT}$ .

The extraction studies will be initiated by measuring the extent of  $\text{Me}_2\text{DBT}$  removal from a hexanes solution of  $\text{Me}_2\text{DBT}$  that is thoroughly mixed with a solution of  $(\text{NH}_3)_5\text{Ru}(\text{OH}_2)^{2+}(\text{BF}_4^-)_2$  in water. Because  $(\text{NH}_3)_5\text{Ru}(\text{OH}_2)^{2+}$  is sensitive to air-oxidation to  $\text{Ru}^{3+}$ , which has a very low affinity for thiophene ligands, it will be necessary to

conduct the extraction studies in an inert atmosphere such as Ar; a  $H_2$  atmosphere will also be tried because the hydrotreated feed will have a  $H_2$  atmosphere as it enters the proposed extraction process. The extent of  $Me_2DBT$  extraction will be determined by GC analysis of the hexanes phase.

In order to recycle the  $Ru^{2+}$  complex after it has been coordinated by  $Me_2DBT$ , the aqueous solution containing the  $Ru^{2+}$ - $Me_2DBT$  complex will be treated with a coordinating and inexpensive gas such as  $N_2$ , ethylene, or  $CO$ . Equilibrium binding affinities of these gases will be determined in order to evaluate the best conditions for recycling the  $Ru^{2+}$  complex.

A second operational mode for the extraction of hindered DBTs will be developed by adsorbing the  $Ru^{2+}$  onto insoluble supports such as silica or alumina. In this mode the hydrotreated feedstock will be passed through a column of  $Ru^{2+}/SiO_2$  or  $Ru^{2+}/Al_2O_3$ . The hindered DBTs will adsorb on the supported  $Ru^{2+}$ , thereby yielding the very low-sulfur petroleum fuel. Recycling processes for the  $Ru^{2+}/SiO_2$  and  $Ru^{2+}/Al_2O_3$  adsorbents will be developed using displacing gases, in a manner similar to that described for the solution extractions.

Although  $Ru^{2+}$  is chosen for these investigations because of its documented affinity for dibenzothiophene, there is some evidence that  $Fe^{2+}$  is also able to bind these molecules. Therefore, similar extraction and adsorption studies will be pursued with  $Fe^{2+}$  complexes. Successful development of these new processes would lead to the production of gasoline and diesel fuels with much lower sulfur content than is possible using current hydrotreating technology.

## **ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT**

This is a new project, and no results have been communicated.

### **Students Supported Under this Grant**

Scott McKinley, a Ph.D. graduate student in chemistry

Dr. Celedonio Alvarez, a postdoctoral associate from Oviedo, Spain